MECHANICAL PROPERTY ENHANCEMENT OF PVP-PVA NANOCOMPOSITE BY GRAPHENE OXIDE

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Supervisor's Certificate

This is to certify that the work presented in this dissertation entitled ″**MECHANICAL PROPERTY ENHANCEMENT OF PVP–PVA NANOCOMPOSITE BY GRAPHENE OXIDE**″ is a record of original research carried out by **Sanu Shaw** under my supervision and guidance in partial fulfillment of the requirements of the degree of **Master of Technology** in **Ceramic Engineering**. His thesis, in my opinion, is worthy of consideration for the award of degree of Master of Technology in accordance with the regulations of the institute. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any degree or diploma.

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Abstract

Graphene, is the building block of many carbon forms, including graphite, carbon nanotubes and Buck-minster fullerenes. It has honey-comb lattice structre with an atomic layer of sp^2bonded carbon atoms. Its excellent properties for example, like Youngs modulus is about 1 TPa, breaking strength is about 140 GPa, thermal conductivity is about 5000 $Wm^{-1}K^{-1}$, and high specific surface area of about 2650 m^2g^{-1}. One of the most important application of graphene is in the fabrication of layered polymer nano-composites. Its unique two dimensional morphology provides high available surface area with very small thickness (in nano size) which can be exploited in load bearing, electrical, and barrier applications. However, the reinforcing agents and their types, considerably enhance crystallinity, microstructure, and glass transition of the composites. Therefore, underpinning the processing-microstructure-property relationship in these materials is very important. The easier route of graphene production is through the top-bottom approach, where graphene oxide (GO) is synthesized by chemical exfoliation method followed by suitable reduction of GO to graphene. GO can hold various oxygen containing functional groups that make it easily mixed in nonpolar solvents. Subsequently, by deffreant chemical treatments, few of those functional groups can be removed, and few others can be added/created, and the layer-matrix attachment can be done. The current work focous on the approaches to strengthen the matrix-reinforcement interface by various types of amines, resulting in unbelively ultra-strong and ultra-tough PVA and PVP nanocomposites. The enhaned mechanical properties were investigated by tensile testing of different graphene oxide samples and chemically reduced ghaphene samples (reduced by TEA and TEOA). It has been confirmed that the reduced graphene sample shows better elastic properties compare to GO based polymer composites.

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CHAPTER 1:

INTRODUCTION

1. Introduction

In this chapter, we briefly discuss the latest advances in interface control performance as a function of graphene structures in polymer nanocomposites. And then broadly define the scope of the current survey. Graphene is defined as monolithic sp2 hybrid carbon atoms arranged in a honeycomb lattice structure. It is a basic component of a different allotrope, including graphite, carbon nanotubes or Buckminister fullerenes. Due to the high strength of the covalent bonds between the carbon atoms, the graphene has excellent tensile strength (~ 125 GPa) and Young's modulus (~ 1000 GPa) [1], making it the most robust material known Steel strong. In addition, these carbon atoms themselves have high conductivities of high thermal conductivity (5000 Wm-1K-1) [2] and (~ 200,000 cm2 V-1 s-1) [3], and the graphene is assigned to the best thermoelectric conductor. Unlike carbon nanotubes or bark balls, graphene sheets carry only all of the carbon atoms on the surface of the sheet, providing a large theoretical surface area (2630 m2 / g). These properties of two-dimensional thin plates prepared with high tensile strength provide graphene for applications such as flexible electronics, quantum capacitors, hydrogen storage devices, chemical sensors and nanocomposites. [4-6].

Carbon nanocomposites with carbon-based fillers have opened up materials development and research fields, mainly using graphite (limited degree), carbon fiber, expanded graphite, carbon black, carbon nanofibers and granular nanostructured carbon. Thus, a modest improvement in mechanical properties has been achieved. The use of carbon fibers has been shown to improve the macroscopic properties of polymer composites. Mainly by the polymer in the development of filler network, these fillers tend to gather to reduce the strength of composite materials. Treatment of modified graphite with a strong acid results in a peeled graphite library that can accommodate functional groups as well as contain polymer chains. A polymer such as poly (styrene-methyl methacrylate copolymer), PMMA polymer blended with polyvinyl chloride (PVC), poly (lactide) or polystyrene (PS) Of the improved mechanical properties in which the tensile strength is

improved compared to the pure polymer. Further improvement is achieved by using carbon nanotubes as a filler. However, their partial dispersion in the polymer matrix is found to affect the mechanical properties of the developed composite material. Efforts to establish suitable load transfer conditions have been observed by changing the processing technology and surface functionality in the manufacture of composite materials. Examples of this type include electrospinning the polymer-GC blend to enhance the orientation and interaction between the polymer and the filler, resulting in enhanced compressive strength. Similarly, the orientation and tensile strength of the polymer nanocomposites are improved in the poly (vinyl chloride) polymer matrix with styrene-functionalized CNTs. Although CNT acts as a filler to produce higher mechanical strength than other graphite fillers, the unique combination of graphene strength, maximum Young's modulus and two-dimensional morphology makes graphene an ideal choice for reinforcing materials in high performance polymer composites.

The graphene has a significant advantage over other fillers because it extends to a large length and width of only 0.34 nm in thickness (up to several nanometers in the case of several layers of graphene). It can not be split, in the direction of the plane to produce the greatest power. Its large area of the surface to strengthen the interface with the matrix, so as to design a lot of opportunities for the interface. The graphene in the polymer matrix has the same properties as the filler with the same micron level. For example, a stripped graphite sheet synthesized from an alkali metal-graphite intercalation compound (GIC) can be used as a filler in polyethylene or polypropylene to increase the rigidity of the finished product. In addition, graphene-derived fillers can exhibit rigidity, strength and strain-failure, which substantially exceeds the stiffness, strength and strain-destruction of conventional micron diameter carbon fibers. The micrometer graphite sheet approaches the critical crack size, resulting in early failure, while the graphene filler is several orders of magnitude thinner than the graphite sheet. This prevents the early destruction of the composite material and promotes the improvement of toughness and ductility. Thus, graphene-based fillers have been used to make novel, tough and functional polymer composites. However, these

nanostructured additives profoundly affect the polymer morphology and microstructure, resulting in improved performance, and the more detailed study of the processing-structure-performance relationships of these composites is fundamentally necessary.

The original graphene does not have any defects or functional groups, which makes it difficult to disperse in the aqueous system. This limits the full use of graphene sheets. Several means have been used to control the macroscopic properties of the material by adding or removing the polymer matrix before or before the addition of the polymer matrix. Alternative routes include custom graphene oxide, which is an intermediate that processes graphene from graphite from a chemical route. Such a route is interesting because it provides an opportunity to enhance performance in a water-processable aqueous polymer system. The Lerf-Klinowski model shows that the graphene oxide produced by the Hummers or modified Hummers process produces structures with hydroxyl and epoxy groups with a high base area and a carboxylic acid group at the edge of the sheet（Figure 1.1）[7] a graphene oxide-based peeling method produces large-sized side panels that can be chemically functionalized and dispersed in the polymer matrix and further deoxidized to produce new composite materials.

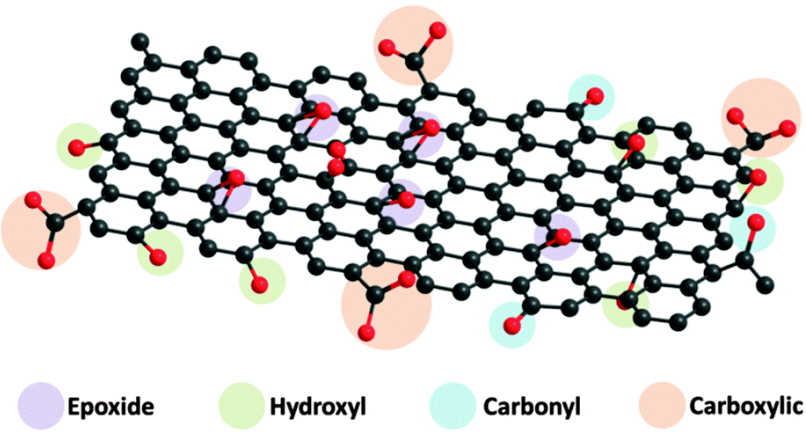


Figure 1.1 Lerf Klinowski model displaying functional groups on graphene oxide, containing epoxide, hydroxyl, carbonyl and carboxylic groups.（Adapted from Chem. Commun., 2016,52, 72).

The stripped graphene oxide produced by the heat or sonication process provides a form having a different transverse dimension. The hot-stripped graphene（TEGO） sheet

contains residual oxygen groups and exhibits wrinkled organoid morphology with a transverse dimension of only several hundred nanometers. Such corrugated nanosheets embedded in the polymer matrix are dispersed in the polymer matrix but produce a property enhancement of about 2% by weight at higher weight fractions [8,9]. Similarly, the sonication process provides a well-peelable sheet in the solvent, but the sheet of the sheet is again reduced to several hundred nanometers, thereby preventing the aspect ratio of the large area of graphene sheet. Mechanical agitation is another way of using large lateral size graphene sheets. However, relatively low yield and slow flaking procedures show that GO can be explored and scattered alternative pathways. These changes in the lateral dimensions and microstructures of the graphene oxide sheets result in varying degrees of interfacial interlocking and adhesion to the polymer matrix resulting in a different degree of performance enhancement.

With respect to the dispersion of graphene in the polymer matrix, several ways have been used to utilize the peeling and stabilization of the filler prior to addition. (In situ or in situ) in the polymer matrix, thereby controlling the macroscopic properties of the material. Isocyanate-treated graphene oxide stripping is a functionalized graphene oxide platelet that exhibit stable dispersions in polar solvents. Similarly, GO is dispersed in acetone, and subsequent multi-step functionalization of graphene in the epoxy resin matrix has been successful in producing systems with enhanced mechanical properties. In addition, the polystyrene polymer inserted into the functionalized graphene sheet increased its elastic modulus and tensile strength by 58% and 70% of its pure polymer. The epoxy resin embedded in functionalized graphene increased the flexural strength by 48% and its thermal stability and glass transition temperature were further improved.

These studies show that the intrinsic filler properties strongly affect the structural-to-performance relationship of polymer nanocomposites. They play a major role in graphene polymer nanocomposites because they profoundly affect the chemical, thermodynamic, interfacial and morphological characteristics of segmented polymers. The optimum composite properties are typically achieved by adjusting the preparation conditions and / or

by functionalizing the filler. In most cases, functionalization improves the mechanical properties of the graphene-based polymer system. These elements preferentially form supramolecular complexes with enhanced interfacial adhesion and dispersibility of graphene in the polymer matrix. A number of polymerization systems have been observed that have various routes for dispersing graphene in a matrix with improved mechanical properties. Functionalized carbon-based fillers range from 0.1 to 5 wt. % Shows a 30-350% increase in the modulus of elasticity of different polymers such as nylon-6, poly (methyl methacrylate) PMMA, poly (vinylidene) (PVDF) and epoxy resins and an increase in tensile strength of about 50 -200%. In general, various improved mechanical properties can be achieved by incorporating graphene fillers by changing the interface of the different polymerization systems.

Poly (vinyl alcohol) (hereinafter referred to as PVA) polymers exhibit a sensitive mechanical property for the incorporation of non-functionalized graphene fillers. For example, 0.7% by weight of graphene oxide-containing PVA polymer improves the tensile strength. On the other hand, an improvement in tensile strength was observed for a 1.8% filler load. Functionalized graphene bound to the polymer matrix also exhibits enhanced mechanical properties. In essence, the tensile strength and the elastic deformation rate of the composite material can be varied several times in the polymer matrix by using certain functions. For example, the PVP-stabilized reduced graphene bonded to the PVA matrix exhibits an improved strength of 0.7% by weight of the carrier. Fill the amount of filler. Subsequently, a sulfonated graphene sheet was added to the PVA matrix and produced a tensile property of 117% under a 3 wt% graphene filler.

Ideally, the graphene sheets incorporated into the polymer matrix should be present as rigid disks or platelets in the polymer matrix. However, it has actually been observed that the graphene sheet follows a curved or shrinking platelet-like structure in the polymer matrix. These curved structures in the polymer affect the crystallinity of the polymer matrix. It is shown that the graphene sheet in the polymer matrix tends to roll up when heated above its glass transition temperature. If there is strong compatibility between the polymer and the

graphene sheet, the rolling effect is suppressed to a high temperature, resulting in a more expanded conformation. However, if the affinity between the polymer and the graphene sheet is reduced, the sheet will produce a more pleated or rolling form. The retention or change in the form of the filler can affect the microstructure and properties of the material and the ability to control these microstructures can lead to qualitative properties. In addition, most of the polymer crystallinity is also affected by the addition of the filler as a nucleation site that affects the crystallization rate and the crystal growth rate. However, the degree of influence on crystallinity is a function of the form of the filler, its functional groups, and the polymer matrix.

Gradual understanding has evolved, taking into account the extra volume elements in addition to the two phases of the matrix and filler in the nanocomposites. These are present in the interface between the filler and the matrix, and can evolve into tens of nanometers thicker volume elements. It has been found that the interface controls many of the properties of polycrystalline ceramics and metal systems. Likewise, evidence is also evolving, and these areas also occur in polymer nanocomposites. The quantitative assessment of such interphase regions in polymer nanocomposites depends on the interaction between the polymer and the filler. The interfacial region of the polymer extends completely to the polymer chains in the matrix with a mobility that exceeds the interface hundreds of nanometers. Such an interface may have properties and structures different from the bulk polymer and may alter the properties of glass transition, crack propagation, electron transport and load transfer.

These studies show that differences in mechanical properties can be attributed to several factors, including filler morphology, their degree of dispersion or uniformity, orientation and interfacial adhesion. Thus, the salient problem with the region of the polymer / GO composite is to understand the inherent properties of the dispersed state of the GO filler in the polymer matrix, the interaction of the interface, the crystallinity of the segmented polymer, and the influence of all of these parameters in the composite The microstructure of the material.

CHAPTER 2:

LITRERATURE REVIEW

2. Literature review

2.1 Polymer composites

For a long time, humans have become familiar with the art of composite technology. Are composed of two or more constituent materials having different properties, i.e., a matrix and a reinforcing material, which are formed by the integration of these components to form new materials having their own set of properties. First, straw-reinforced mud tiles and concrete were prepared, including the addition of straw or loose stone / gravel in the cement matrix to enhance the strength of the composite. These materials are traditionally used for the construction of buildings, roads, bridges or houses. Other examples of composites include metal composites, ceramic composites, and polymer composites. These are used to make automobile body, swimming pool, storage tank, household appliances and electronic equipment. Due to these examples of composite materials developed in modern engineering, they are classified as fiber reinforced polymer composites (FRP) and glass reinforced polymer composites (GRP). They consist of a polymer matrix (which is a thermoplastic or thermosetting composition) embedded with different fillers or reinforcing materials, such as staple fibers or long fibers or laminates, or granules such as glass, carbon or aramid.

2.2 Polymer nanocomposites.

Since the 1990s, nanocomposite systems have been widely used. Since then, the problem has grown rapidly, taking into account different substrates, including metals, ceramics and polymers. Although metal and a lower degree of ceramic matrix for the application of nanocomposites, but the polymer matrix nanocomposites has been an important area of research.

Thus, according to standards defined in ISO/TS27687 (2008), the nanocomposites are distributed as:-

1) One-dimensional (1D) nanofiller: nanotubes and nanofibers with diameter lower that 100nm;

2） Two-dimensional （2D） nanofiller: in the form of plates, laminates or shells with a thickness less than 100 nm.

3） Three-dimensional （3D） nanofiller: iso-dimensional nanoparticles such as nanometric silica beads with all dimensions less than 100 nm.

In order to prepare nanocomposites with better mechanical properties, we need systems with lower filler content to provide better interfacial interactions. Therefore, we transferred to a nanofiller with a size of less than 100 nm to achieve enhanced performance. This is achieved by using nanostructured fillers such as carbon nanotubes or graphene in modern trends.

2.3 Graphene as fillers

Graphene is the youngest member of the carbon family. Which is an allotrope of carbon having two carbon atoms （2D） arranged in a honeycomb-like lattice. In the structure, it is responsible for building all the graphite structure. Graphenols are laminated together to form graphite with a layer spacing of 0.334 nm. In addition, the extended honeycomb structure is rolled to form 1D nanotubes and encapsulated to form a 0D fullerene-type structure [10] （Figure 2.1）.

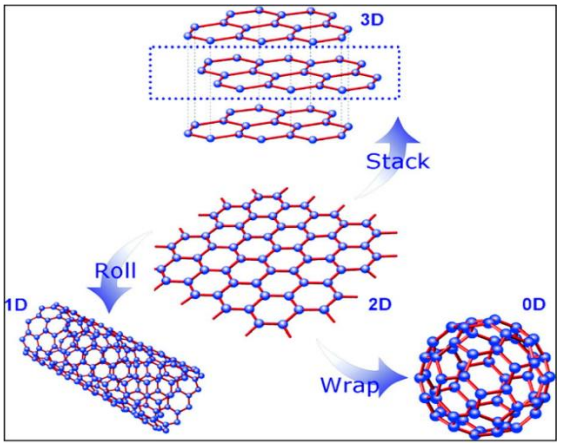


Figure 2.1. The building block of all graphitic structures.

For the first time in 2004, Geim Group attempted to produce monolithic graphene by simply cutting the adhesive tape into graphite crystals [11]. Statistically, a 1 μm thick graphite sheet was dispersed onto a single layer of thin sample, which was a very simple and effective method. Soon, by supporting the thermal growth of graphene on a metal or metal

carbide substrate by using carbon-rich carbon-rich surfaces or hydrocarbons vapor-deposited, two different mechanisms were used to develop support for growth on solid substrates Type method. Although these growth methods produce wafer-grade graphene, the low yield is limited to electrical applications. Gradually, large-scale production of graphene became a necessity, and the chemical route reconsidered the new challenge of converting graphene oxide into graphene through a multifunctional reduction process.

Brodie and Hummers' extensive works produce large polyaromatic hydrocarbons (PAH) as submicron tablets of graphite. The precise structure of the atoms of these graphene segments provides the absolute accuracy of the edge structure of the nanoscale graphene domains. Brodie works on the oxidative intercalation of potassium chlorate in concentrated sulfuric acid and nitric acid to produce modified graphite sheets consisting of highly re-hybridized carbon sheets containing hydroxyl and carboxyl moieties. The suspension was originally named graphite acid, but was soon referred to as oxidized graphite (GO). After his work, Hummers soon reported a faster and safer graphite oxide route [12], in which graphite was dispersed in a mixture of concentrated sulfuric acid, sodium nitrate and potassium permanganate (instead of potassium chlorate) at 45 ° C Stir for several hours. X-ray diffraction studies of graphite oxides show that the typical disappearance of the graphite interbedded diffraction peaks (0.334 nm) and the new appearance of larger interlayer spacing (0.65-0.75 nm) [13]. The graphite intercalation compounds obtained by inserting sulfuric acid between the graphite layers are commonly used in chemical, electrochemical and industrial applications. After the graphite is inserted through one of these methods, little or even monolithic material is obtained by decomposing the inserted reactants to produce a large amount of gas in the van der Waals space by chemical or thermal methods. Thus, their route has proven to be a multifunctional method for mass production of graphene, making it useful in a variety of applications

Similarly, the graphene oxide produced by the Hummers or modified Hummers method has a hydroxyl structure and has a higher concentration of epoxy groups on the base surface and has a carboxylic acid group around the sheet. SEM analysis showed that the presence of carboxyl groups at the outer boundaries of the sheet produced a larger transverse pleat shape.

Such fillers in the polymer matrix may have strong interlock properties that affect mechanical properties. On the other hand, the stripping of the graphene oxide produced by the heat or ultrasonic treatment method provides a form having a different lateral dimension. It has been found that the suspension produced by sonication reduces the lateral dimension of several hundred nanometers [14].

2.4 Reduction of graphene oxide.

The physical properties of graphene oxide are very different from graphene. The graphene oxide is decorated with oxygen-containing groups on its surface, making it highly soluble in water or polar solvents and chemically insulated. It is to be noted that the graphene has a conjugate structure of the recovered π-network so that it is only dissolved in the non-polar solvent and is conductive. The restoration of the conjugated structure is an important aspect of the application of graphene, the main reason is to improve the conductivity, high mechanical strength, optical or thermal properties. This indicates that the restore process is one of the most important conversion processes.

The reduction can be achieved by chemical [15], heat [16] or electrochemical treatment [17]. A typical strong reducing agent such as hydrazine hydrate [18], water alkyd [19], sodium borohydride [20] or sodium hydride [21] is commonly used to oxidize graphene oxide Reduced to graphene. However, while chemically reduced graphene has several advantages, the continuing challenges of these methods involve a large extent or defect, shrinkage, residual functional groups or tendencies due to attractive van der Waals forces.

For example, the use of hydrazine as a reducing agent causes the accumulation of N-charge and the formation of hydrocarbons by the reaction of the carboxyl group. Secondly, hydrazine is highly toxic, resulting in a very high aggregation of the reduced product. Therefore, the selection of suitable reducing agents becomes an important parameter to reduce. Song et al. (2012) demonstrated that the use of different reducing agents such as hydrazine hydrate, HI and NaBH4 had few reductions. Their results show that HI reduction produces less aggregated GO films, good flexibility and improved tensile strength, whereas

NaBH4 and hydrazine produce rolled GO films that are rolled up and decomposed into blocks [22] (Figure 2.2).

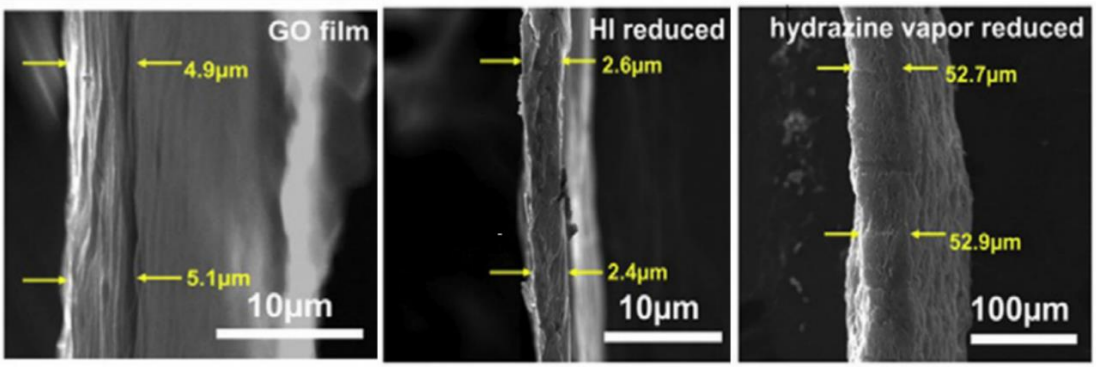


Figure 2.2. Different types of graphene obtained by using different reductants

2.5 Graphene-based polymer composites

Graphite-based polymer composites have become the most important and interesting areas of research for the past few years. The incorporation of polymers into graphene shows the luxury properties of nanocomposites developed. Some researchers have reviewed the preparation and performance of this volume of graphene composites. This nanocomposite material has opened up a large number of applications from the fields of energy, heat transport and biology. Its excellent electrical or mechanical response has been indicative of graphene as a fundamental alternative to conventional packing in the manufacture of polymer nanocomposites.

Cai et al. (2009) showed that the Young Modulus and Hardness values were significantly increased by about 900% and 327%, respectively, combined with 4.4 wt. Percentage of graphene nanosheets in polyurethane polymers. Their results show that there is a strong interaction between the graphene and the polyurethane (PU) polymer due to the formation of chemical bonds, allowing for effective load transfer [23].

Zhen et al. (2010) show that the addition of caprolactam to nylon-6 polymer has a tensile strength of only 0.1% by weight (56 to 123 MPa) for nanocomposites grafted on nylon-6 polymers [24].

Miller et al. (2010) improved the covalent bond between GO and epoxy polymers by the yield of coupling agents, increasing the elastic modulus by 30% and the elastic modulus at 50% without affecting the toughness of the resin [25]

Zhao et al. (2010) examined the mechanical enhancement due to the dispersion of the filler, which is a function of the volume fraction (V) / weight fraction (w) of the graphene filler. They discussed the increase in tensile strength from 17 to 43 MPa when the graphene loading increased from 0% (equivalent to pure PVA polymer) to 1.8%. The filler loading increased further to 3%, increasing the tensile strength, but the elongation at break decreased from 212% of pure PVA to 98% of the composite. After discussion, the non-monotonic nature relates to the progress of uneven dispersion of graphene inclusions from time to time during the increase in filler content. At lower filler levels, the graphene nanosheets are uniformly dispersed in the matrix, providing linear and rapidly changing mechanical properties. However, once the filler content exceeds its critical value, the smaller distance between adjacent graphene sheets forces them to bind due to van der Waals interaction between the sheets. (Figure 2.3). This is accompanied by end-to-end interaction, partial overlap, and even flat recovery. Since the dispersion of PVA-graphene becomes uneven and the mechanical properties become weak [26]. This aspect is necessary to understand the strengthening mechanism of polymer composites.

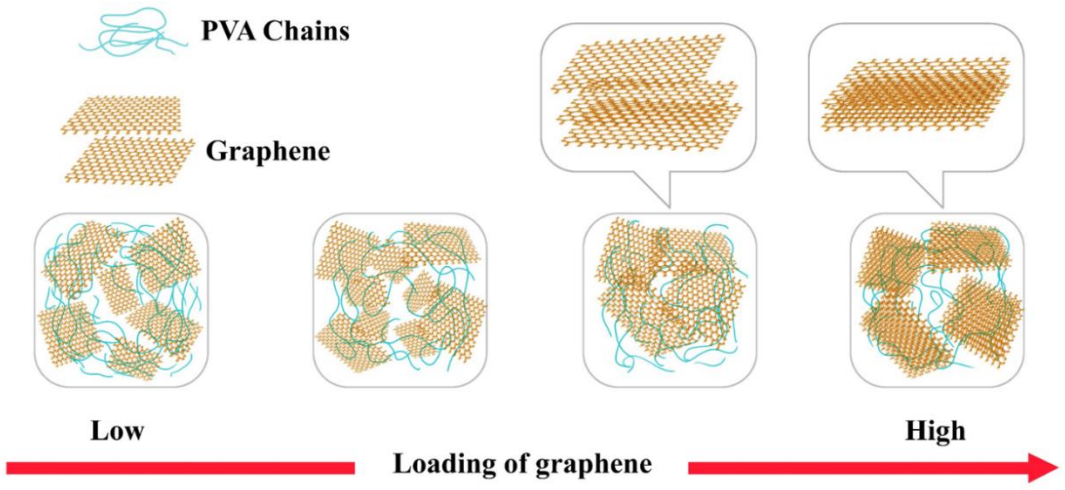


Figure 2.3. Nature of dispersion of graphene filler loading in a polymer matrix.

Xiao et al. Examined the effects of GO and PVP on the hydrophilicity, porosity and porosity of the membrane. The graphene oxide (GO) and polyvinylpyrrolidone (PVP) were introduced into the poly (vinylidene fluoride) (PVDF) film, and the phase inversion technique was induced by impregnation. The results showed that GO and PVP showed synergistic effect in controlling the hydrophilicity, morphology and porosity of the composite membrane. PVDF / PVP / GO composite membrane at the same time to achieve a large number of enhanced hydrophilicity and porosity. In addition, the effect of GO content on the morphology and porosity of the composite membrane was also studied. It was found that increasing the GO content not only caused a significant change in the pore morphology, but also caused an increase in the porosity of the composite membrane.[27]

2.6 Challenges

Although graphene and graphene derivatives are very successful as fillers; the understanding of the basic principles of the interface of the filler matrix, the reasons for the improvement of strength and toughness, and the mechanism of load transfer still exist in many areas. In addition, as previously described, nanocomposites may not be modeled solely on the basis of micromechanical methods involving the properties and geometries of the matrix and filler. The importance of the interface that has been pointed out in graphene / PMMA systems can not be overlooked. The interfacial shear stress is consistent with the van der Waals force interaction between the matrix and the filler, indicating that the weak dispersion also mediates the interaction between PMMA and monolayer graphene platelets. The simple graphene / polymer system indicates that the weak dispersion of the fact that this interface can be modified by esterification and / or amidation to impart covalent or other stronger interactions, thereby increasing the interface shear stress.

2.7 Scope and objective of the work

The work of large-scale natural graphite crystal derived graphene oxide and its functional form as a filler, polyvinyl alcohol and polyvinyl pyrrolidone as a matrix. The choice of PVP and PVA as a waterborne processable polymer model system is of technical importance. The filler content has been intentionally selected in the low range of (0.2-

0.8% GO） to observe the various properties of the transition. The effects of several amines on the aqueous colloidal stability of graphene oxides have been studied, dispersed in the polymer system and the composites were prepared. For mechanical properties. The composite membranes have been evaluated by uniaxial methods and the results have been discussed in the overall context of the physical and chemical properties of the composites.

CHAPTER 3:

MATERIALS AND METHODS

3. Materials and Methods

In this part various synthesis,sample fabrication methods are brifly discuess.

3.1 Fabrication of PVP-PVA nanocomposites

Various set of PVP（LOBA Chemie）and PVA（LOBA Chemie） nanocomposites were prepared by conventional solution casting method,to fabricate PVP and PVA nanocomposites 0.75 gm of PVP and 0.75 gm of PVA wear dissolved in 50 ml Deionized water at 95°C under reflux for 6hours to form an aqueous solution. Finally, 10 ml of the as prepared homogeneous PVA-PVP colloid were poured onto glass petri dishes and kept in a vacuum at 40 °C for 48 hours to form PVA-PVP composite films. The films were then peeled off the substrate for further characterizations. The prepared films typically had 90-120μ thickness

3.2 Fabrication of graphene oxide reinforced PVP- PVA nanocomposites（PPGO）

0.75 gm of PVA and 0.75 gm of PVP ware dissolved in 30 ml deionized water at 95°C under reflux to form an aqueous solution. Separate solutions of GO with varying vol%（0.2 to 0.8 GO） were sonicated in 20 ml DI water to form a yellowish-brown colloidal solution. The obtained GO solutions were mixed with PVA-PVP under vigorous stirring for about 2 hours at 60 °C to form PVA-PVP-GO（50 ml） colloids. The PVA-PVP colloid is comparatively thicker than the GO colloid, which makes the mixing of the two components difficult and does not mix instantly. Therefore, vigorous stirring of the aqueous GO mixed PVA-PVP colloid is required to ensure complete and uniform mixing. Finally, 10 ml of the as prepared homogeneous PVA-PVP-GO colloids with different concentrations were poured onto glass petri dishes and kept in a vacuum at 40 °C for 48 hours to form GO reinforced PVA composite films. The films were then peeled off the substrate for further

characterizations. The prepared films typically had 100-120μ thickness. (A typical process of fabricating the composites is shown in Fig.3.1)

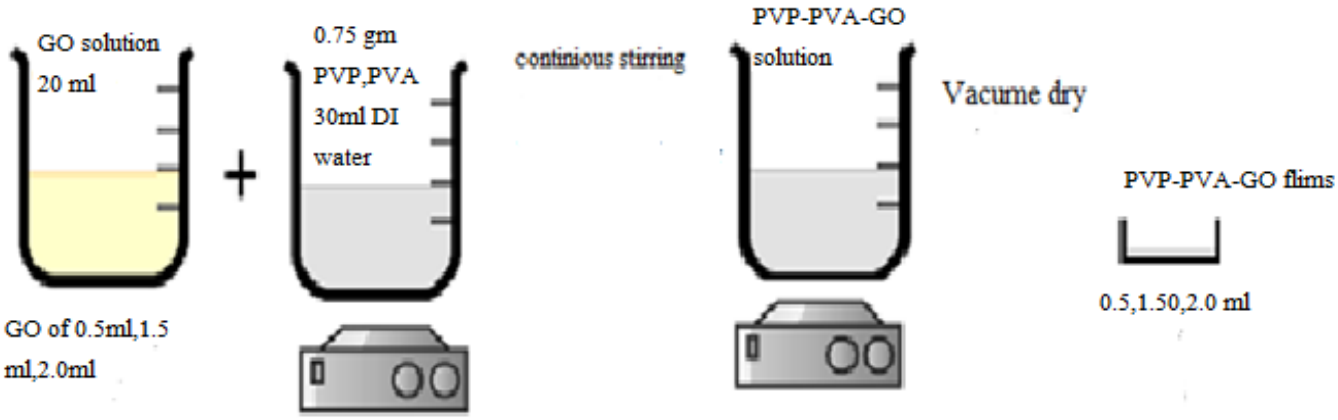


Figure 3.1 Method of fabrication of PVP-PVA-GO films

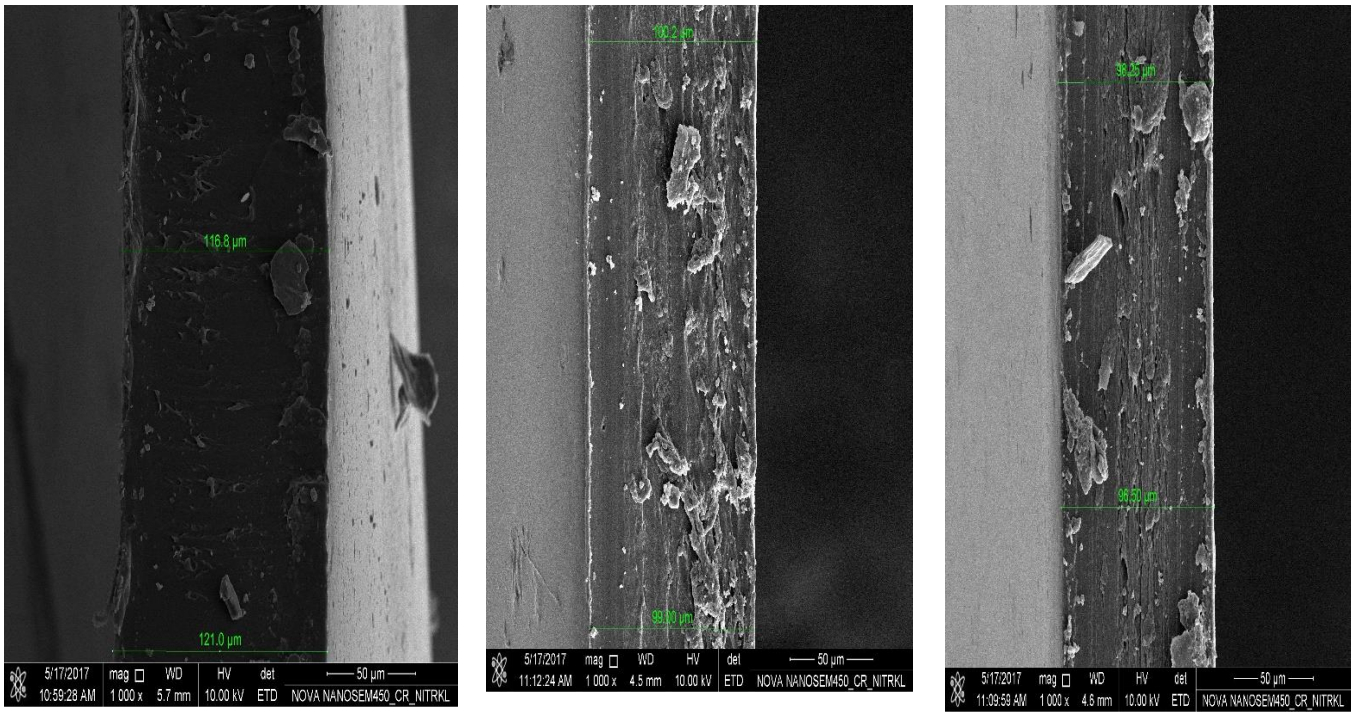
3.2.1 Fabrication of triethylamine (TEA) reduced GO reinforced PVP-PVA-GO flims (PPGTA)

50ml of the PVA-PVP-GO blend along with 50μl of TEA (LOBA Chemie) was refluxed for 24 hours to obtain a uniform TEA reduced PVA-PVP-GO colloid. Castings of the blend were made by dropping 10 ml of the colloid on glass petridish and kept for drying at 40°C until weight equilibrium. The cast films were peeled off the petri dish for further characterization.

3.2.2 Fabrication of triethanolamine (TEOA) reduced GO reinforced PVP-PVA-GO flims (PPGTO)

50 μl TEOA (LOBA Chemie) was added to the 50ml PVA-PVP-GO blend and refluxed for 24 hours to obtain a uniform TEOA reduced PVA-PVP-GO colloid. The black colored colloid was similarly cast onto glass petridish and dried at 40°C. The films were peeled off the glass and used for further characterizations.

Important parameters considered for the drying of the colloid were the drying temperature and the type of substrate used for casting the solution. It was observed that when the colloids were dried in an oven at temperatures of 60 ^{O}C or 80 ^{O}C, it resulted in shrinking, cracking, and wrinkling of the films in all types of composites. Besides, when the colloids were cast onto a plastic petri dish, the drying was not so uniform. It had occasional pinholes in the films, and the film was highly wrinkled.



PVP-PVA films GO reinforced PVP-PVA films Reduced GO PVP-PVA films

Figure 3.2 FESEM image of crosssectional view of different films.

CHAPTER 4:
RESULTS AND DISCUSSIONS

4. Results and Discussions

4.1 Tensile Strength Test of PVP-PVA and GO Reinforced PVP-PVA Composite Film

Mechanical properties of PVA-PVP and GO reinforced PVP- PVA composite films with a filler content of 0.2, 0.6, 0.8 % were calculated using universal testing machine (UTM),then from the result the stress and the strain of the samples are calculated and from those stress,strain we plot graphes between sterss vs strain, which is shown in figure 4.1. Based on the obtained plot, different mechanical properties like tensile strength, elastic moduli and yield strength were calculated (Table 4.1).

Table 4.1. Mechanical property evaluation of PGO

Sample Name	Young Modulus (Gpa)	Ultimate Strength (Mpa)	Elongation at break (%)	Yield Strength (Mpa)
PVP-PVA flims	1.58±0.33	43.53±7.29	32.21	37.46±6.32
PPGO-0.2	1.18±0.14	43.12±2.87	24.34	40.97±2.56
PPGO-0.6	1.2±0.09	59.1±1.51	15.24	51.22±3.27
PPGO-0.8	1.78±0.1	72.79±8.94	8.46	66.69±6.56

The pristine PVP-PVA flims shows good stiffness of 1.58 GPa and the ultimate strength of 43.53 MPa which is typical value of PVP-PVA composite (although for same polymer with different molucular weight can have different tensile properties).In the other hand the reinforced composite shows improved mechanical strength as the filler loading is increased from 0.2 to 0.8 %. For the PPGO-0.2 the elastic modului and ultimate strengths are 1.18 GPa and 43.12 MPa. For PPGO-0.6, the elastic modului and ultimate strengths are 1.2 GPa and 59.1 MPa.When the filler loading increased to 0.8%, it shows huge increase in mechanical properties. Elastic modulus becomes 1.78 GPa (~13% increase) and the ultimate strength is increased upto 72.79 MPa (almost double of PVP-PVA flims).These

enhancement has done due to strong van der wall force which is present in the GO reinforced polymes ,and also GO have excellent mechanical strength（which is describe in introduction part）,but in case of pure PVP-PVA films the van der wall force is abcent.These values are considerd to be good as introducing very small amount of GO in polymer matrix shows great imporvement in mechanical strength.

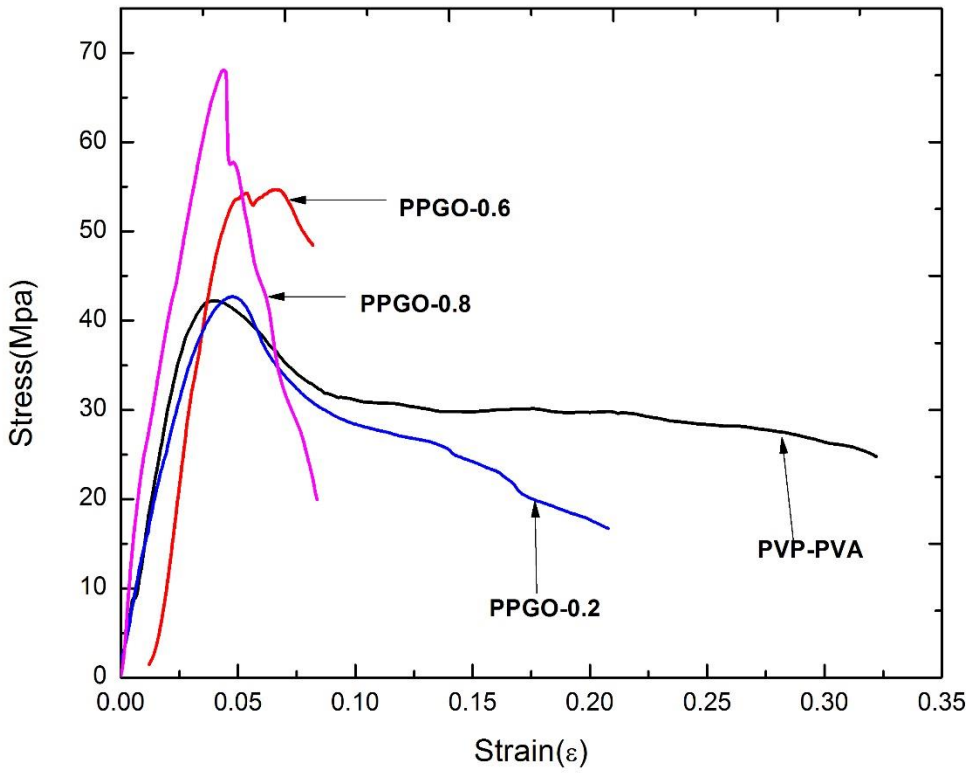


Figure 4.1： The Stress-Strain curve of PPGO

Figure 4.1 shows the stress-strain relation of PVP-PVA and GO-reinforced PVP-PVA Composite films. It can be observed from the figure 4.1, that the pure PVP-PVA film composite has the least stress bearing capacity. That means it has least tensile strength （43.53 MPa）, while PVA-PVP reinforced with 0.8 % shows the best strength （72.79 MPa）. That concludes, as the filler amount increases the stress absorbing capacity i.e. mechanical strength increases. This is due to increase in total van der walls force acting in

between polymer and filler. As we are increasing the filler amount the more GO provides more van der walls force providing better tensile strength.

In this work the filler loading is very low when we compare to the other research paper,to see the change in mechanical properties and still we can see the improvement in elastic modulus and ultimate strength and we can also see that the polymer became more brittle.

4.2 Tensile Strength Test of Reduced GO Reinforced PVP-PVA Composite Film

Mechanical properties of TEA and TEOA reduced GO reinforced PVP- PVA composite films with a filler content of 0.2 % were calculated using universal testing machine (UTM),then from the result the stress and the strain of the samples are calculated and from those stress,strain we plot graphes between sterss vs strain. which is shown in figure 4.2. Based on the obtained plot, different mechanical properties like tensile strength, elastic moduli and yield strength were calculated (Table 4.2).

Table 4.2： Mechanical property evaluation of PPGTA and PPGTO

Sample Name	Young Moudulus (Gpa)	Ultimate Strength (Mpa)	Elongation at break (%)	Yield Strength (Mpa)
PPGO-0.2	1.18±0.14	43.12±2.87	24.34	40.97±2.56
PPGTO-0.2	0.89±0.37	28.76±8.16	169.5	23.56±6.89
PPGTA-0.2	1.32±0.04	37.23±2.05	89.13	35.47±1.76

In case of chemicaly reduced GO flims we could not find great improvement in mechanical strength but we can observe that the elasticity of the modified composite is improved remarkably. When we compare those values with PPGO-0.2 we can observed that the TEOA reduced modified films have quite low young modulus value but the elasticity is increase remarcable.This is due to the reduction which made the TEOA reduced polymer

more elastic but the stiffness is low.When we compare between TEA reduced films and PPGO films here we can see diffarent properties, like in TEA reduced films stiffness or young modulus is high from PPGO-0.2 and the elasticity is also increase,but not as PPGTO films. So we can conclude that TEOA increase the elasticity, thats why other mechanical properties goes down.Where as for TEA we can see slight improvement in mechanical properties.

In case of TEA reduced GO reinforced PVP-PVA film composite (PPGTA-0.2) shows better mechanical properties than TEOA reduced GO reinforced PVP-PVA film composite (PPGTO-0.2) but PPGTO-0.2 have shown better elastic property than PPGTA-0.2. For PPGTA-0.2 the maximum elongation is 89.13 %, the elastic modulus and tensile strength are 1.32 GPa and 37.23 Mpa respectively. For PPGTO-0.2, the elongation reported is 169.5 %, which is more than 6 times of PPGO-0.2 flims. The elastic modulus and the tensile strength were reported as 0.89 Gpa and 28.76 Mpa.

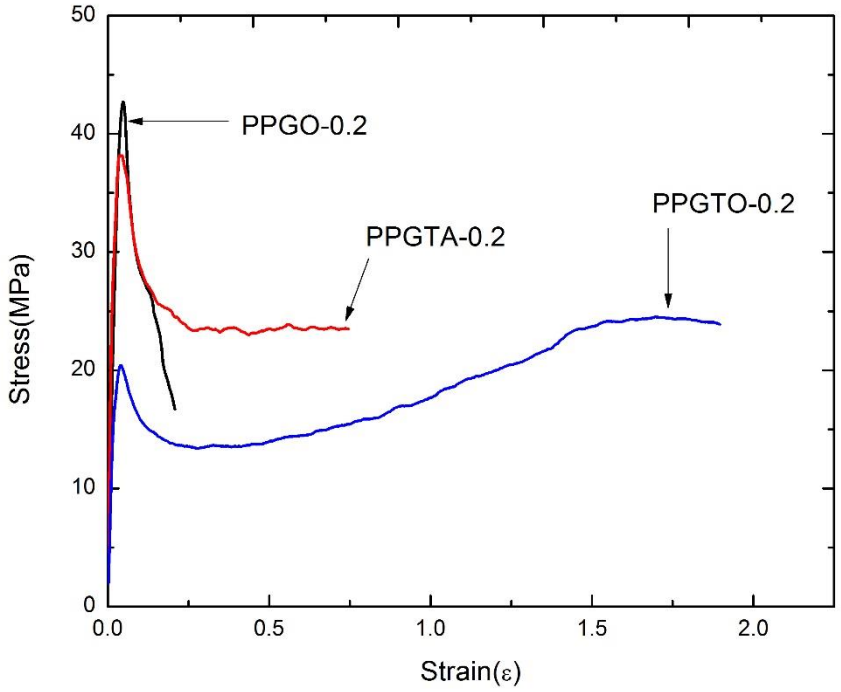


Figure 4.2. The Stress-Strain curve of PPGTA and PPGTO

Figure 4.2 shows the stress-strain relation of PPGO-0.2 and reduced GO-reinforced PVP-PVA Composite films. It can be observed from the figure 4.2, that the pure PPGO-0.2 film composite has the least elasticity while reduced TEOA reduced GO reinforced film composite shows the best elasticity. In PPGTA, only strong van der walls force is present while in the case of PPGTO strong van der walls force as well as strong hydrogen bonds are present. The reason behind the better elasticity of TEOA reduced GO reinforced composite film is the presence of intermolecular hydrogen bond between hydroxyl group and oxide group of GO. Due to presence of hydrogen bonding in PPGTO, it has better resistance against deformation.

4.3 Morphology and Microstucture

Cross section of fractured samples are observed under FESEM. The morphology and the microstructure revels some interesting infromation of composites.

The FESEM image of tensile fracture surfaces with pure PVP-PVA composite is shown in Fig. 4.3（a）. A smooth fracture surface is seen in Fig. 4.3（a） at 10000· magnification, which indicates an elastic fracture.

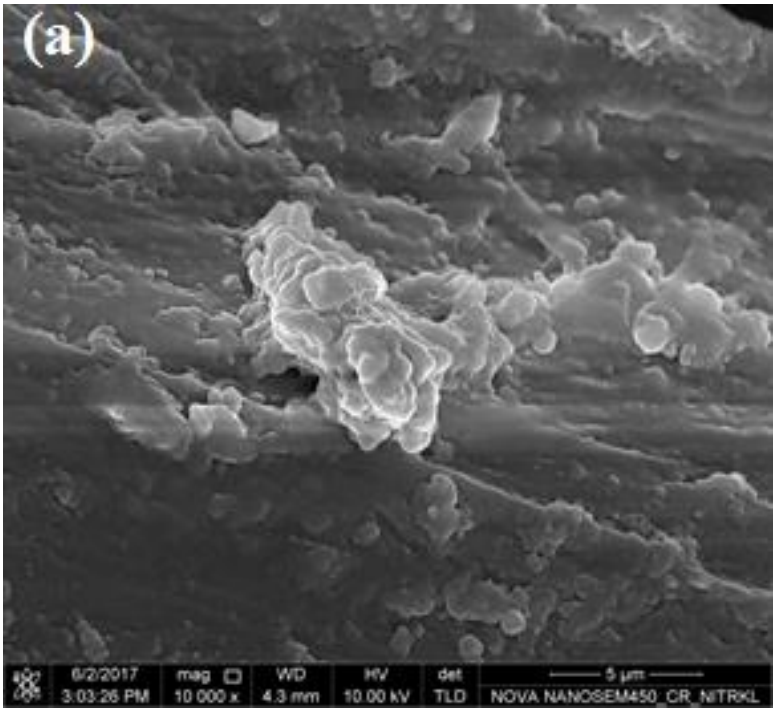


Fig. 4.3(a) FESEM micrograph of PVP-PVA composite.

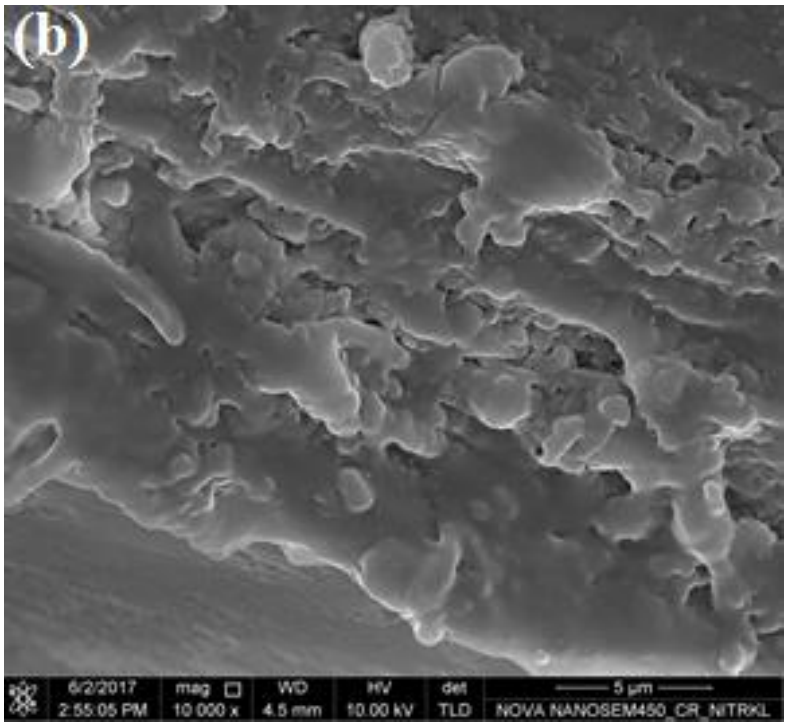


Fig. 4.3(b) FESEM micrograph of GO reinforced PVP-PVA composite.

Fig. 4.3 (b) shows how with 2.0 ml GO, the fracture surface becomes cloud-like and rough. GO has a high specific surface area. Also, the adhesion with the matrix is very sturdy. Thus, GO addition enhances the strength of the composite.

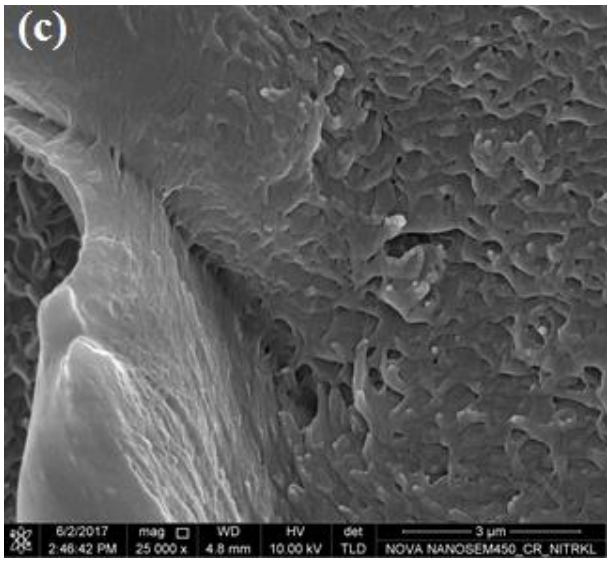


Fig. 4.3(c) FESEM micrograph of TEA reduced GO reinforced PVP-PVA composite

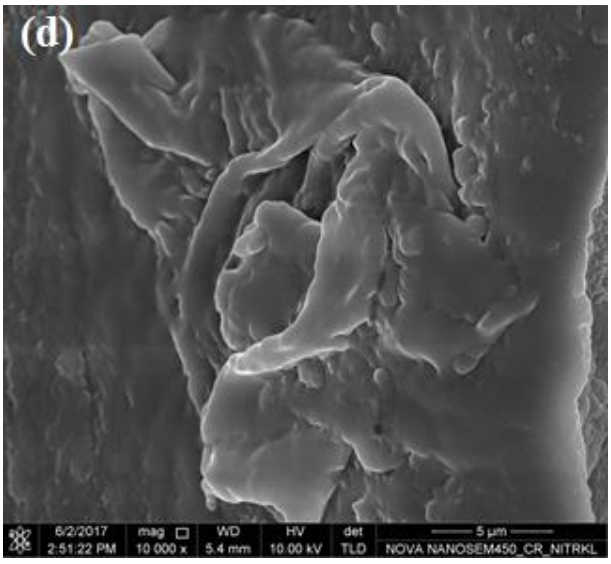


Fig. 4.3(d) FESEM micrograph of TEOA reduced GO reinforced PVP-PVA composite.

Fig. 4.3(c) shows the cross-section of the fracture surface of the PGTA-0.5 composite after a tensile test. It is clear from the FESEM image that GO is generally dispersed properly in the matrix. Upon uniaxial tension the PVP-PVA matrix are strained but the GO resists the strain in the direction of the tension, and enhances the strength and the elastic property of the film composite. Fig. 4.3 (d) shows the microstructure of the PGTO-0.5 film composite surfaces after the tensile test which shows same property as PGTA film do. The pull-out of the GO in the PGTO matrix is also seen to be decrease.

CHAPTER 5:
SUMMARY

5. Summary

We have succesfully prepared the GO reinforced PVP-PVA polymer composit of filler loading varying from 0.2% GO to 0.8% GO. We have also prepared triethanolamine(TEOA) and triethylamine(TEA) reduced GO reinforced PVP-PVA polymer composit of filler loading 0.2% GO . The samples were prepared by solution casting,then solution are kept into glass patridish followed by drying. Dried samples were cut in proper dimension for the tensile testing. The tensile test data provides the stress vs strain cruves which were drawn by origin software. The analysis of stress vs strain cruve helps in calculating the mechanical properties like Young modulus(E),Maxmimum strength,Elesticity and Yield strength of the smaples. After a fair comparisn of diffrent samples, we concluded that GO reinforcement to PVP-PVA polymer improves the strength and the young's modulus values. The young's modulus and the strength of the smaple were reported as 1.58 GPa and 43.53 MPa respectively, whereas for 0.8% GO reinforced PVP-PVA polymer composit the Young modulus and the Strength of the samples were found to be 1.78 GPa and 72.79 MPa respectively. The total increase in Young modulus and strength was reported as ~13% and ~67.21% respectively. Based on the obtained results, it is clear that, for a very less amount of filler loading, can cause a huge improvement in the composite's mechanical properties. So we can increase the GO amount to get a good enhancement in mechanical properties. These enhancement reported in it's mechanical properties is due to the intermolecular van der wall forces and other reason is, the excellent mechanical properties of GO. Comparetive data of the TEA and TEOA reduced GO reinforced PVP-PVA polymer composite revels that a great improvement in elasticity although strength and Young's are almost same. We can find a huge enhancement in elastisity TEOA samples compared to the TEA reduced GO film composite. The TEA reduced smaple has stronge van dar wall force compair to pure PVP-PVA composite which provides a good resistance against deformation, whereas in TEOA reduced composite films a strong van der wall froces acts along with an additional hydrogen bonding which causes TEOA more elesticic compared to TEA reduced GO film composites.

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